An investigation of Ozone formation through its precursors (CO; NOx; VOC) and its loss at a sub-urban site of Agra

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INTRODUCTION

Ozone is a secondary pollutant (Sebald et. al., 2000; Eubanks et al., 2009) that at the surface is considered as a photochemical oxidant pollutant, formed from series of chemical reactions in presence of sunlight. About 90% of atmospheric ozone is present in the stratosphere, and only 10% is present in the troposphere.The Intergovernmental Panel on Climate Change (IPCC, 2001, P7) suggested a 36% increase in global tropospheric ozone since the industrial revolution.

Ozone plays an important role in atmospheric processes and can positively or negatively influence human health and the environment depending on its location in the atmosphere. Ozone in the stratosphere filters out harmful ultra-violet radiation from the sun, protecting life on earth.

In the lower troposphere ozone is considered a dangerous pollutant that negatively influences human health and ecosystems (EPA, 2006; Paoletti et. al., 2006; Gurjar et. al., 2010), being a key constituent of urban smog it is responsible for increased susceptibility to diseases, reduced growth and reproductive capacity and reductions in crop yields (Mauzerall and Wang, 2001). In plants ozone is responsible for impaired photosynthesis, protein and chlorophyll degradation, and changes in metabolic activity (Booker and Fuhrer et. al., 2009).

Ozone is also the third most important greenhouse gas (Fuhrer and Booker, 2003; Forster et. al., 2007; IPCC, 2007; Racherla et. al., 2008). Due to its oxidizing capacity, it is the major source of hydroxyl radicals (OH°), it generates by photolysis of ozone in the troposphere by the solar ultraviolet radiation near 300 nm followed by reaction with molecules of water.

$O_3 + hv \longrightarrow O(^1D) + O_2, \lambda < 330$ nm

$O(^1D) + H_2O \longrightarrow 2OH^{\circ}$,

Reactions with OH° radicals initiate the oxidations of many other atmospheric trace gases (e.g., hydrocarbons) consequently removing them from the atmosphere (Guicherit and Roemer, 2000; Staehelin et. al., 2001).

The Ozone concentration is regulated by complex phenomena (Jenkin and Clemitshaw 2000; Finlayson – Pitts and Pitts 2000). O_3 exists in the troposphere via two processes: (1) Downward

transport from the stratosphere (Stratospheric-Tropospheric Exchange) (Ganguly and Tzanis, 2011) and (2) Photochemical production through the oxidation of CO, CH_4, non-methane hydrocarbons (NMHCs) and other volatile organic compounds (VOCs), controlled and catalyzed by NOx (NO & NO_2) (Jonson et al., 2006). Between this, photochemical production dominates (Vukovich, 1973).

Chapman (1930) first proposed the fundamental ozone-forming and destruction reactions in the stratosphere. These reactions are now known as the Chapman cycle:

$O_2 + h\upsilon\ (\lambda < 242\ nm) \longrightarrow 2O$

$O + O_2 + M \longrightarrow O_3$

$O + O_3 \longrightarrow 2O_2$

$O_3 + h\upsilon\ (\lambda << 336\ nm) \longrightarrow O(1D) + O_2$

In troposphere Ozone formation is initiated by the reaction of various VOC or CO with the OH° radical, this is followed by the conversion of NO to NO_2 (through reaction with HO_2 or RO_2 radicals), which also regenerates OH°. NO_2 is photolyzed to generate atomic oxygen, which combines with O_2 to create O_3.

$VOC + OH^{\circ} \xrightarrow{[O2]} RO_2 + H_2O$

$CO + OH^{\circ} \xrightarrow{[O2]} HO_2 + CO_2$

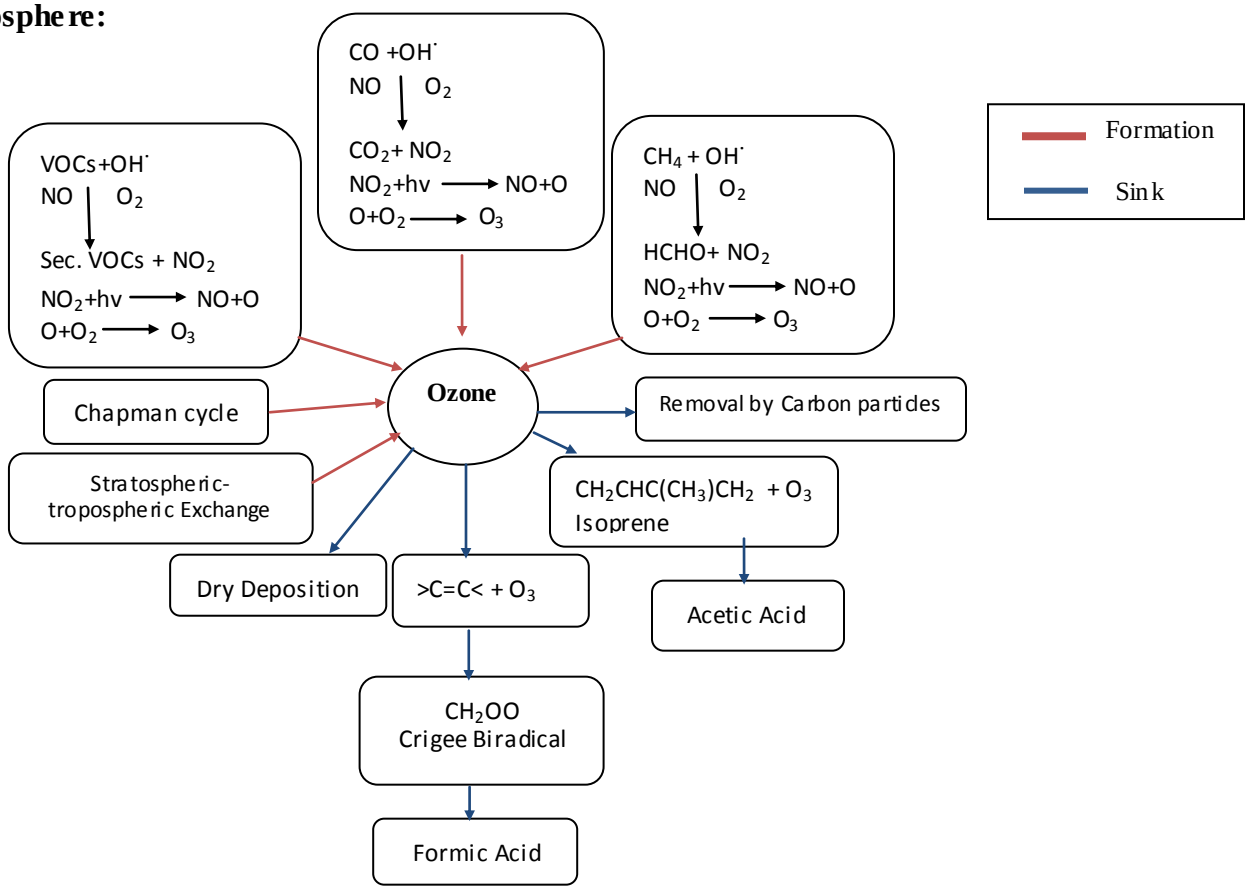
$RO_2 + NO \xrightarrow{[O2]} \text{Secondary VOC} + HO_2 + NO_2$

$HO_2 + NO \longrightarrow OH^{\circ} + NO_2$

$NO_2 + hv \longrightarrow NO + O$

$O + O_2 + M \longrightarrow O_3 + M$

The schematic diagram shows the different process of formation and loss of ozone in the troposphere:



The residence time of O_3 in the atmosphere is long, enabling long range transport over hundreds to thousands of kilometres, thus allowing occurrence of high ozone levels at both regional and urban scale (San Jose et. al., 2005). The development of mathematical tools to predict ozone concentration is very useful because it can provide early warnings to the populations and reduce the number of measurement sites.

Meteorology plays an important role in air pollutants formation, dispersion, transport and dilution. Therefore, the variations in local meteorological conditions, such as wind direction, wind speed, temperature, and relative humidity, can affect the temporal variations in O_3 and its precursors (Dueñas et al., 2002; Satsangi et. al., 2004; Elminir, 2005; Singla et. al., 2011).

Ozone Precursors:

1. Carbon monoxide (CO): It is mainly emitted from incomplete combustion of fossil fuel and biomass burning, while oxidation of methane (CH_4) and volatile organic compounds (VOCs) can

significantly contribute to the atmospheric budget of CO (Jaffe et al., 1997; Holloway et al., 2000). Emissions of CO from global biomass burning sources show strong seasonal and inter-annual variations (van derWerf et al., 2006). Reaction with the hydroxyl (OH) radical is the primary sink of CO in the atmosphere. In the troposphere, the reaction between CO and OH represents 90-95% of the CO sink, and about 75% removal of OH (Noveli et al., 1998).

2. Nitrogen Oxides (NOx): The combustion of fossil fuels in motor vehicles is one of the major sources of anthropogenic NOx in most cities (Cofala et. al., 2007b). The other manmade sources of NOx include electric utilities, industrial, commercial, and residential sources that burn fuels (EPA, 2003). NOx emissions are also produced naturally by bacterial and volcanic activity and lightning (Schumann & Huntrieser 2007).

3. Volatile organic compounds (VOCs): They are defined as compounds with vapor pressure greater than 133.3 pa (1 mm Hg) at room temperature. Volatile organic compounds (VOCs) are gaseous non-methane organic compounds (NMOCs) with carbon atoms of C_2 to C_{12} (Nguyen 2009).

Volatile organic compounds (VOCs) are important precursors to the formation of ground-level ozone, and hence photochemical smog (IPCC, 2007). VOCs react with hydroxyl radical (OH°) through photochemical reactions to produce oxygenated compounds, and subsequently form ozone (Na et. al., 2003; Hofzumahaus et al., 2009). The relation between ozone, nitrogen oxides (NOx) and VOCs is driven by complex nonlinear photochemistry.

Oxidation products of VOCs can contribute substantially to Secondary organic aerosol (SOA) formation through nucleation and growth processes (Zhao et al., 2005a, 2006; Levitt et al., 2006; Zhang et al., 2012). It is well established that SOA accounts for a significant portion of atmospheric particulate matter (Fan et al., 2006; Carlton et al., 2009; Hallquist et al., 2009; Zhang et al., 2009; Ziemann, 2011), which exert a significant impact on climate (IPCC, 2007) by directly interacting with solar and terrestrial radiations and modifying cloud microphysical properties (Li et al., 2005; Tie et al., 2003, 2005; Zhang et al., 2007).

In addition, some VOCs are also considered hazardous pollutants. For example, 1,3-butadiene and benzene, commonly found in industrial and vehicular emissions, are known carcinogens (USEPA, 2009, 2012). Therefore, it is important to identify the VOC sources and photochemical transformation characteristics, in order to formulate appropriate pollution control policies.

Ozone formation is a highly nonlinear process in relation to NOx and VOC. There is also an analogous split into NOx-sensitive and NOx-saturated chemistry in the troposphere. High VOC/NOx ratios corresponding to NOx-sensitive chemistry and low VOC/NOx ratios corresponding to VOC-sensitive chemistry (Sillman et. al., 2003). In VOC-sensitive regime nitric acid represents the dominant sink for odd hydrogen. In NOx-sensitive regime peroxides represent the dominant sink for odd hydrogen. In NOx-sensitive regime rate of ozone formation increases with increase in NOx concentration. While in VOC-sensitive regime rate of ozone formation increases with increase in VOC concentration.

Ozone Sinks:

Ozone loss in the troposphere can be possible by different pathways it interacts with mineral aerosol, gaseous species (Bonasoni et al., 2004), suspended particulate matter (Singla 2012) and Black carbon (Swamy et. al., 2012, Sharma et. al., 2013). Another possible pathway of loss of ozone is ozonolysis of biogenic and anthropogenic alkenes to form organic acids like Formic acid and Acetic acid (Neeb et. al., 1997).

Black carbon (BC) is a heat absorbing aerosol, is a product of incomplete combustion of fossil fuel, biomass, agricultural waste and forest fire. BC has been found to have a large effect on photochemistry derived pollutants such as ozone (Li et al., 2005). The soot deposited on plant leaves also reduces plant productivity (Bergin et al., 2001). The photolysis rate is generally reduced due to absorption by carbonaceous aerosols, particularly in the early morning and late afternoon with a high aerosols optical path. BC absorbs solar flux and is the second largest contributor to global warming after the green house gases (Jacobson, 2002). BC aerosols cause direct radiative forcing ranging from 0.27 to 0.54 W m^{-2} (IPCC, 2007).

The morphology, size, chemical composition of particles and capacity to carry potentially toxic substances (such as organic substances or metallic compounds) adsorbed on the particle surfaces play a crucial role in adverse effect on health and environment (Senlin et al., 2008). Particulate matter is responsible for human health problem, especially respiratory diseases, visibility reduction and climate change (Kanakidou et al., 2005). Emissions of the particles specially less than 2.5 μm are of greater concern since they are small enough to penetrate into the lungs, where they may exacerbate conditions such as bronchitis and asthma.

In India, particle pollution has increasingly become a severe problem due to fast industrialization and urbanization in the past two decades. Major cities of India are highly polluted by particles (CPCB, 2007).

Organic particles have their major contribution to total mass of fine particles, but they are the least studied and analyzed fraction of aerosol due to this complex nature. Organic acids are ubiquitous chemical constituents of the troposphere. Weak organic acids could contribute 40% - 60% to the free acidity in precipitation at urban site of Sao Paulo, Brazil (Fornaroa and Gutz, 2003), Since carboxylic acids are highly water-soluble, they have the potential to modify the hygroscopic properties of atmospheric particles, they contribute to both the acidity of precipitation and could act as condensation nuclei (CN) and cloud condensation nuclei (CCN) (Yu et. al., 2000).

Low molecular mass carboxylic acids (LCAs) are a group of organic compounds containing in their structure one or more carboxylate functions (-COOH) and a short hydrocarbon group which can be aliphatic, aromatic, saturated or unsaturated, straight chain or branched.

The occurrence and abundance of carboxylic acids in atmospheric particulate matter depend on meteorological conditions and characteristics of the ambient atmosphere.

Many different sources have been proposed. Direct emissions from the vegetation (Kesselmeier et. al., 2001), ants (Chebbi et. al., 1996), biomass burning (Goode et al., 2000; Christian et al., 2003; Yokelson et al., 2009), biofuel (Yevich et. al., 2003) and anthropogenic combustion sources like vehicles and stationary sources (Perola et. al., 2011; Freitas et. al., 2012; Mkoma et. al., 2014;) may occur.

The room temperature rate constants for the reactions of O_3 with some alkenes are many orders of magnitude smaller than those for the corresponding OH reactions, the fact that tropospheric ozone concentrations are so much larger makes these reactions a significant removal process for the alkenes (Pitts and Pitts, 2000). The formation proceeds through ozonolysis of an alkene forming a Criegee intermediate which quickly rearranges to a carboxylic acid. The reaction with ozone, which is rate determining, is slowest for ethene ($k = 1.7*10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}) and relatively fast for 2-methylbutene ($k = 493 *10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}) (Atkinson, 1990). Isoprene, a non methane hydrocarbon which accounts for ~30–50% of biogenic emissions (Guenther et al., 2006), is also a source of formic acid from products of its photooxidation. Recent experimental evidence suggests, however, that the photooxidation of hydroxyacetone which is one of the products of photooxidation of isoprene produces significant amounts of acetic acid (Butkovskaya et al., 2006) at low

temperature. Ozonolysis of various monoterpenes also yields formic and acetic acid (Lee et al., 2006). Ozonolysis of marine biogenic emissions has been suggested to provide a source of formic and acetic acid (Baboukas et al., 2000).

Wet deposition is thought to be the most important sink of formic and acetic acid (Chebbi and Carlier, 1996). Formate and acetate are collected from mineral aerosols (Lee et al., 2000, 2002; Russell et al., 2002; Falkovich et al., 2004;).

The present study aims to explain ozone formation from its precursor species (NO_x, CO & VOCs) and its loss in the form of organic acids and by black carbon.

LITERATURE REVIEW

The seasonal and diurnal variations of surface ozone and its precursors and the related meteorology have been extensively studied around the world, particularly in Europe (Chatterton et al., 2000; Dueñas et al., 2002) and in North America (Raddatz and Cummine, 2001; Lehman et al., 2004). In recent years, O_3 chemistry has received increased attention in Asia owing to rapid economic and industrial development, accompanied by its increasing air pollutants emissions. The temporal variations of O_3 have been reported at many sites including rural, urban, coastal and mountain sites in India (Lal et. al., 2000; Nair et. al., 2002; Debaje et. al., 2003; Naja et. al., 2003; Satsangi et. al., 2004), Japan (Tsutsumi and Matsueda, 2000; Saito et al., 2002), and Thailand (Pochanart et al., 2001; Zhang and Oanh, 2002).

The mean concentration of O_3, NO, NO_2 and CO over a three year period from January 2000 to February 2003 at an urban site in Nanjing, China are 20.4±18.3 ppbv 10.6±24.5 ppbv, 18.8±11.3 ppbv, and 1.13±0.88 ppmv respectively (Tu et. al., 2007). However, mean concentration for O_3, NOx and CO at a residential site in Hong Kong was 32 ppbv, 45ppb and 574ppbv respectively (Guo et. al., 2009). In north-western part of Himalaya monthly average concentration of O_3 showed distinct seasonal variations with maximum in summer (55.9 ± 9.3 ppb in May) and minimum in winter (30.0 ± 6.2 ppb in January) (Sharma et. al., 2013).

The diurnal variation of O_3 shows a typical pattern for polluted urban areas, characterized by high concentrations during daytime and low concentrations during late night and early morning (Mazzeo et al., 2005, Tu et. al., 2007, Singla et. al., 2011, Im et. al. 2013).

Precursors, NO, NO_2, CO, CH_4 and NMHCs, showed an almost opposite diurnal variation pattern to O_3 at an urban site in China (Jun Tu et. al., 2007). The high mixing ratios of NOx during the morning and evening hours were mainly attributed to the vehicular emissions (Harley et. al., 2005). At an urban site of Mexico, Zheng et. al., 2013 reported that all aromatics reach daily maximum before noon and are consumed rapidly in the afternoon and diurnal variations of the aromatics are strongly correlated with each other, indicating similar emission sources. Aromatic compounds, such as toluene and benzene, are mainly emitted from vehicle exhausts because of incomplete combustion and fugitive fuel evaporation (Na et al., 2003), which explains the pronounced rush hour peak at about 8:00 AM. Since aromatics are relatively reactive with OH (at 298 K, $k_{toluene}$ = 5.63 *10^{-12} cm^3 $molecule^{-1}$ s^{-1}, $k_{benzene}$ =1.22*10^{-12} cm^3 $molecule^{-1}$ s^{-1}, and $k_{C8_aromatics}$ = (7.0-23.1)* 10^{-12} cm^3

molecule^{-1} s^{-1} (Calvert et. al., 2002; Molina et. al., 1999; Suh et. al., 2002). Isoprene is strongly influenced by solar radiation and ambient temperature (Guenther et. al., 2000). The increase of isoprene concentration after midday indicates a natural biogenic contribution (Borbon et. al., 2001).

At an urban site of China the mean concentrations of O_3 in different seasons follow the order of spring>summer>autumn>winter. Meteorological parameters play very crucial role towards ozone concentration. The O_3 concentration showed significant positive correlations with both temperature and wind speed but a significant negative correlation with relative humidity in most months (Tu et. al., 2007). Singla et. al., 2011 reported maximum concentration in summer followed by winter, post-monsoon and monsoon seasons at an suburban site Agra, India, while at urban site in Pearl River Delta, China mean ozone concentration is highest in autumn than summer due to stagnant weather conditions (Shao et. al., 2009). Nishanth et. al., 2012 reported highest O_3 concentration in winter (44±3.1) ppbv while lowest in monsoon (18.5±3.5) ppbv at a rural coastal site at Kannur, India, the highest O_3 observed in winter is attributed to a lower mixing height that results in trapping of pollutants near the earth's surface due to temperature inversion (Debaje et. al., 2006). Similar patterns of seasonal variations have also been observed at a tropical rural site at Gadanki, India (Naja et. al., 2002), a tropical coastal site at Thumba, India (Nair et. al., 2002) and Anantapur, Trivandrum (Reddy et. al., 2010) in south India. In contrast to O_3, the precursors had significant negative correlations with both temperature and wind speed but significant positive correlations with relative humidity in most months at an urban site in China (Jun Tu et. al., 2007) and at semi-urban site in Kullu, India (Sharma et. al., 2013).

Shao et. al., 2009 observed at an urban site in Pearl River Delta (PRD), China, in contrast to O_3, the precursors, NO_2, NO, and CO, show higher concentrations in winter but lower concentrations in summer. Guo et. al., 2007 observed in Hong-Kong seasonal variation of VOCs, toluene concentration is highest in winter at urban and suburban sites considering that there is more photochemical consumption of toluene in summer due to a higher abundance of the hydroxyl radical (OH) however at rural site its concentration is highest in summer, this is likely related to higher evaporation of fossil fuel in summertime. Other measured hydrocarbons such as ethane, ethyne and benzene had the same seasonal trends as toluene at urban and suburban sites. The above seasonal patterns of toluene and other VOCs are consistent with those from other studies at urban sites in Hong Kong (So and Wang, 2003, 2004; Guo et al., 2004a).

Despite showing seasonal and diurnal variation O_3 also shows weekly variation. In Santiago, Chile elevated summertime ozone concentration was found on Sunday compared with Monday-Friday (Seguel et. al., 2012), this is known as weekend effect. This is probably associated with the decreased volume of vehicular traffic and, consequently, lower fresh NO that destroys O_3. Similar effect was seen by Swamy et. al., 2012 in Hyderabad, India but mainly in winter and monsoon period. The lowest weekday/weekend O_3 concentration difference of 1.1 ppbv was observed in June (Summer) while higher variation 8.1 ppbv was observed in July (Monsoon). This effect is pronounced at traffic site as reported by Im et. al., 2013 in Istanbul, Turkey, high ozone concentration on weekends at traffic site, while at rural site ozone concentration is high on weekdays and this is in agreement with the findings of Sadanaga et al. 2008 and Pudasainee et al. 2010 they reported relatively lower weekend effect in rural areas compared to urban and traffic areas.

Depending upon concentration of NOx and VOCs, ozone formation is NOx sensitive and VOC sensitive, when the formation of ozone is VOC-sensitive, the HNO_3 concentration is mostly greater than 3.5 ppb or the O_3/ HNO_3 ratio is below 30 (Sillman and West, 2009). The H_2O_2/HNO_3 ratio points to NOx-sensitive chemistry if the ratio is between 0.2 and 1 (Sillman and He, 2002; Sillman and West, 2009). According to Orlando et. al., 2010, in atmospheres with VOC/NOx ratios smaller than 5.5, NOx reacts preferentially with hydroxyl radicals, removing them from the system and delaying O_3 formation. Therefore, less NOx would be present in the atmosphere. OH• would react with VOCs to form peroxide radicals, which in turn would allow the formation of O_3.

Guo et. al., 2004 used principal component analysis and absolute principal component score technique to find out source profile of VOCs and CO, results show that 65% of total VOCs emission and 78% of total CO emission is from urban emission and biofuel burning. Biomass burning and biogenic emissions contributed to 18% of the total CO emissions, 11% for benzene at a rural site of China.

However, Guo et. al., 2007 reported that air masses in rural areas are more aged than that in urban areas, which leads to less titration of O_3 and more reaction time among VOCs and NOx for the generation of O_3. Additionally, elevated levels of highly reactive biogenic species (i.e. isoprene) in rural areas make significant contributions to O_3 formation as compared to anthropogenic VOCs.

The biomass burning emissions consist of enormous amount of O_3 precursors (CO, CH_4 and non-methane hydrocarbons), which undergo a complex chemistry to produce ozone, increase in concentration of these precursors may lead to increase in O_3 concentration. Srivastava et. al., 2013

studied similar phenomenon in Indonesia where an intense biomass burning event was responsible for enhancement of CO and O_3. Seasonal variation in CO concentration due to variation in amount of biomass burning is reported by Sahu et. al., 2013 during a study conducted in Bangkok, Thailand, the average mixing ratios of CO near the surface were ~250 ppbv, 370 ppbv and 340 ppbv during the wet, winter and summer seasons, respectively. However, Guo et. al., 2004 reported highest concentration in summer and spring at a rural site in China.

CO and NOx are mainly released from mobile emission sources. Percentage release of CO is greater than NOx (Tu et. al., 2001). The higher percentage of CO from mobile sources compared with that of NOx is caused by the mobile engines working at low traffic speed. The ratio CO/ NOx is higher in New Delhi, India (Aneja et. al., 2001) associated with the lower average traffic speed (about 20 km/h) in New Delhi (Gurjar et al., 2004). Guo et. al., 2009 observed in Hong Kong when the northerly monsoons were enhanced, the CO levels were dramatically increased, In contrast to CO, the O_3 levels had a decreasing trend with enhanced northerly monsoons perhaps due to the precipitation and the decrease in temperature and solar radiation.

Studies have found that the increasing trend of ground-level ozone (O_3) was related to high anthropogenic VOC emissions (So and Wang, 2004; Chang et al., 2005; Shiu et al., 2007; Zhang et al., 2007, 2008; Wang et al., 2009; Cheng et al., 2010a).

VOCs can be divided into following categories depending upon their source of emission and their nature: Biogenic volatile organic Compounds (BVOCs), Anthropogenic volatile organic compounds (AVOCs), Oxygenated volatile organic compounds (OVOCs) and Nonmethane Hydrocarbons (NMHCs).

BVOCs are primarily emitted from vegetations, BVOCs include terpenoids (e.g., isoprene and monoterpenes), hexenal family compounds (hexenals, hexenols, and hexenyl esters), methanol, and acetone (Guenther et al., 2000). The broad leaf trees and conifer plants are responsible for the emission of terpenes, semiterpenes, and diterpenes, etc. which provide major emission among the natural sources (Wayne et al 2000). Isoprene is known to be emitted from biogenic sources (Jobson et al., 1994) but there are also studies of the contribution of isoprene from vehicular exhaust (Borbon et al., 2001; Barletta et. al., 2002).

AVOCs are released from anthropogenic sources include evaporation of solvents and gasoline (Watson et al., 2001; Chan et al., 2006), petrochemical manufacturing, petroleum refining (Buzcu et. al., 2006), motor vehicle exhaust (Ho et al., 2009; Schauer et al., 2002; Watson et al., 2001) and

biomass burning (Andreae and Merlet, 2001; Schauer et al., 2001). Aromatic compounds, such as benzene, toluene and xylene, are mainly emitted from vehicle exhausts because of incomplete combustion and fugitive fuel evaporation (Na et al., 2003, Ling et. al., 2011). Although BVOCs emission (e.g., isoprene) is the dominant VOC source on a global scale (Guenther et al., 2006), anthropogenic activities are responsible for most of the VOC emissions in and around heavily populated urban areas (Li et al., 2007; Wang et al., 2009; Apel et al., 2010).

Oxygenated organic compounds includes a wide range of organic molecules such as alcohols (R–OH), ketones (R_1–CO–R_2), aldehydes (R–CHO), ethers (R_1–O–R_2), esters (R_1–COO–R_2) and acids (R–COOH). OVOCs are VOCs with short lifetime in the atmosphere. OVOCs are an important fraction of the VOCs and are primarily emitted by vehicular transport, solvent usage and biogenic sources (Placet et al., 2000; Sawyer et al., 2000; Legreid et al., 2007b). Furthermore, several OVOCs are produced by oxidation processes in the troposphere (Atkinson, 2000). Carbonyls (aldehydes and ketones), are one of the most abundant group of OVOCs in urban air (Bakeas et al., 2003; Granby et al., 1997). Short chain OVOCs mainly emitted directly from vegetation as well as being intermediates of the breakdown of other biogenic VOCs (including 2-methyl-3-buten-2-ol, acetone, methanol, cis-3-hexen-1-ol, cis-3-hexenyl acetate, and camphor) (Kesselmeier et al., 2000).

Hydrocarbons with exclusion of methane are sometimes considered as one group: the Non-methane hydrocarbon (NMHCs). Hydrocarbons C_4-C_9 are mainly emitted from gasoline that can freely evaporate at ambient temperatures. Evaporation of gasoline during its distribution not only causes economic loss, but also contributes substantially to VOC in ambient air. According to the European Emission Inventory Guidebook (EEIG) 2009 (updated July 2012, http://eea.europa.eu/emep-eea-guidebook), the contribution of evaporative emissions to total non-methane VOC from road transport ranged from 2.9% to 16.5% for various European countries in 2006.

Aromatic hydrocarbons, usually representing a significant fraction of total NMHCs, are emitted by fuel combustion and evaporation of fuels and solvents. Barletta et. al., 2005 observed ethyne and benzene are usually associated with combustion processes (mainly from automobile exhaust in urban areas); toluene, m-xylene and p-xylene can be emitted from vehicles, but paints and industrial processes (solvent application) are likely additional sources (Na et. al., 2003); and ethane is mainly related to leakage from LPG or natural gas. The concentration of benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene ranged 0.7-10.4 ppbv, 0.4-11.2 ppbv, 0.1-2.7 ppbv, 0.2-10.1 ppbv, 0.2-5.2 ppbv and 0.1-6.9 ppbv respectively (Barletta et. al., 2005). However, Liu et. al., 2000

(benzene = 9.0 ppbv, toluene 17.5 ppbv, ethylbenzene 2.9 ppbv), Barletta et. al., 2002 (benzene = 5.2 ppbv, toluene = 7.1 ppbv) and Na et. al., 2003 (benzene = 1.6 ppbv, toluene =12.8 ppbv, ethylbenzene = 1.8 ppbv) also determined concentration of different VOCs at their sites. Chan et. al., 2002 observed that toluene, benzene and (m+p)-xylene dominated the aromatic VOC concentration in Hong Kong. Toluene had an average concentration of 77.2 μgm^{-3} and a maximum of 320.0 μgm^{-3}. Benzene had an average and a maximum concentration of 26.7 and 128.6 μgm^{-3}, respectively. The (m + p)-xylene also had a fairly high concentration with a maximum of 106.0 μgm^{-3} and an average of 12.1 μgm^{-3}).

Gasoline exhaust was the largest contributor (23%) to the VOC concentration in the PRD, followed by industrial emission (16%), LPG leakage & propellant emission (13%). The vehicle-related emission sources, defined as the sum of gasoline exhaust, diesel exhaust and gasoline evaporation, accounted in total for 40% of the VOC level in the PRD (Yuan et. al., 2013). Other studies reported that aromatic hydrocarbons were much higher in gasoline vehicle exhausts (19.3-49.2%) (Schauer et al., 2002; Liu et al., 2008a; Guo et al., 2011).

Ling et. al., 2011 used Positive matrix factorization and Observation based model (OBM) to identify sources of VOCs in Southern China. Aromatic hydrocarbons such as toluene is applied frequently as a solvent in shoemaking, furniture, adhesives, and printing (He et al., 2002; Chan et al., 2006; Liu et al., 2008a) and benzene is associated with vehicular emissions. Similar results are observed by Tang et. al., 2008 and Louie et. al., 2013 that Toluene, ethylbenzene and the xylenes are emitted from industrial solvent use and gasoline evaporation. Using OBM it was observed that ethene, toluene, m-xylene and p-xylene were mainly responsible for local O_3 formation in the region.

Studies on vehicular exhaust suggest that the ratio of different aromatic compounds (particularly benzene and toluene) can be useful in identifying VOC sources, as benzene is mainly emitted from vehicular combustion and toluene is released from industrial applications. A B/T ratio of around 0.5 (wt/wt) has been reported to be characteristic of vehicular emissions (Chan et. al., 2002). Barletta et. al., 2005 calculated an average value of 0.6 (wt/wt). Higher benzene emissions with respect to toluene have been reported for biofuel and charcoal burning (Andreae and Merlet, 2001), and a B/T ratio higher than 1 has also been reported for coal burning (Moreira dos Santos et al., 2004). In the UK and US, B/T ratio was ranged from 0.2 to 0.7 (Derwent et al., 2000; Baker et al., 2008). A high B/T ratio (0.7) was found for vehicular sources by Tang et al. (2008) in the PRD (Pearl River Delta, China) region, while at PRE (Pearl River Estuary) this ratio was 0.4, lower than that of vehicular

sources (B/T = 0.7), characteristics of having both vehicular and industrial sources. In the EPRD (East PRD) and WPRD (West PRD), B/T ratios were 0.8 and 0.8 respectively, which were slightly larger than 0.7 indicating a strong contribution from vehicular emissions (Louie et. al., 2013).

VOC/Benzene can be used to estimate the relative contributions of stationary and mobile sources of VOC, according to Hoshi et. al., 2008 benzene can be used as reference compound based on several considerations. First, benzene has a considerably low potency of ozone formation (Carter, 2000); its reaction in the atmosphere is known to proceed more slowly than other VOCs. Secondly, more than 90% of benzene was estimated to be released from mobile sources in the Tokyo (Ministry of the Environment, Japan, 2005).

Emission controls on anthropogenic VOCs sources is critical for reducing ground level ozone pollution. Generally, mass-based and reactivity-based approaches form the basis for controlling VOC emissions. The mass-based approach is commonly adopted in the US, UK, Japan and Hong Kong, as the amount of VOCs emission is relatively easier to be quantified. However, the ozone reduction efficiency is limited as photochemical ozone formation is more directly linked to VOCs reactivity rather than the mass of VOCs emitted. For example, recent research has demonstrated that reactivity-based VOCs control could be more effective than the mass-based approach to abate the ozone problem (Derwent et al., 2007; Cheng et al., 2010b). To assess the reactivity and subsequent ozone formation potential (OFP) of various VOCs, a recently updated maximum incremental reactivity (MIR) scale (Carter, 2008) can be used. The aromatic HCs and alkenes, followed by alkanes, are the dominant contributors to OFP. Aromatics and alkenes together consisted of around 80% of the total OFP of VOCs, while alkanes contributed another 12-14% (Louie et. al., 2013). In Foshan, China alkenes played the most important role in O_3 formation and accounted for ~49.5% of total OFP, followed by aromatic hydrocarbons (~28%), alkanes (~20.5%) and acetylenes (< 0.5%) (Tan et.al., 2012).

Biogenic VOCs have significant impact on ozone production and different models have been used to understand the effect of BVOC to ozone formation (Derognat et. al., 2003; Bao et. al., 2010). Im et. al., 2011 used nonhydrostatic model MM5 and Community Multiscale Air Quality (CMAQ) models to investigate impact of anthropogenic and biogenic emissions on surface ozone concentrations. The inclusion of biogenic NMVOC emissions in model runs resulted in improved values of the statistical measures used to evaluate model calculated ozone results. The minimum ozone levels at night time are much better captured by the model as isoprene and terpenes are responsible for an additional

removal of night-time ozone by 3.2 and 14.9 ppb. This result is most probably attributed to the chemical destruction of ozone by isoprene and terpenes (Geyer et al., 2003) while inclusion of biogenic emissions resulted in an increase up to 25 ppb on average in the day-time maximum ozone concentrations.

Though several studies have been conducted on the levels of ozone and its precursors but there are very few which give models to predict ozone concentration. The prediction of ozone concentrations is very important due to the negative impacts of ozone on human health, climate and vegetation. In recent years, different modeling techniques like multiple linear regressions, feedforward artificial neural networks as well as principal component regressions (combining multiple linear regression and principal component analysis) are being used to model ozone concentrations (Abdul-Wahab and Alawi, 2002, Lengyel et. al., 2004, Abdul Wahab et. al., 2005, Goncalves et. al., 2005). Ozone concentrations are very difficult to model because of different interactions between pollutants and meteorological variables (Borrego et. al., 2003). One of the approaches to avoid this problem is multiple linear regression which is commonly used to obtain a linear input output model for a given data set (Abdul-Wahab et. al., 2008) but it faces serious difficulties when the independent variables are correlated with each other. One method of removing such multicollinearity from independent variables is to use the principal component analysis (PCA). However, as ozone in the lower atmosphere is a complex non-linear process, principal component analysis cannot adequately model the non-linear relationships. A new statistical method, artificial neural networks is a well suited method for modeling ozone since it allows for nonlinear relationships between variables (Zheng et. al., 1998).

Ozone loss in troposphere is possible by various means. Bauer et al., 2004 have reported 5% decrease in global tropospheric ozone mass due to heterogeneous reactions on dust aerosol. Singla 2012 showed significant negative correlation between TSP and O_3 (r=-0.71) in Agra, India. This negative relationship between TSP and O_3 reveals lowering of surface O_3 with increase in the concentrations of TSP. Sharma et. al., 2013 reported ozone and black carbon are negatively correlated (r= - 0.42) indicating ozone depletion by surface reactions on BC particles, these soot particles provide a large specific surface area for heterogeneous interactions with reactive trace gases such as O_3, Swamy et. al., 2012 also observed similar effect in Hyderabad.

Ozonolysis of alkenes to form organic acids is also a sink of ozone, which is observed by Qi et. al., 2006 who performed ozonolysis of ethene in dry synthetic air at atmospheric pressure and room

temperature. The typical FTIR spectra of the reaction mixture were recorded and formation of CO, CO_2, HCHO, HCOOH and H_2O_2 was identified. The rate constant for O_3-ethene reaction was found to be k1 = 1.44 * 10^{-18} cm^3 $molecule^{-1}$ s^{-1} which is in good agreement with the results reported by Atkinson, 1997.

According to Guarieiro et. al., 2009 a very special set of conditions are required for complete combustion of fossil fuel, chemicals such as alcohols, carbonyl compounds, carboxylic acids and their respective anions are produced due to incomplete combustion. Similar results have been reported by Khare et. al., 2011 using absolute principal component analysis for source apportionment of organic acids. Author also included secondarily formation from photochemical reactions of anthropogenic hydrocarbons and other precursors in the atmosphere.

Paulot et. al., 2011 estimated the global source of formic and acetic acids were ~1200 and ~1400 Gmol yr^{-1}, dominated by photochemical oxidation of biogenic volatile organic compounds, in particular isoprene. Their sinks were dominated by wet and dry deposition. GEOS-Chem chemical transport model was used to evaluate this budget against an extensive suite of measurements from ground, ship and satellite-based Fourier transform spectrometers, as well as from several aircraft campaigns over North America.

Primary emissions and photochemical transformations were suggested as the major sources of carboxylic acids (Yu et. al., 2000). Studies indicate that formate is largely originated from secondary transformations (Wang et. al., 2007; Mkoma et. al., 2012) and acetate from primary emission (Guarieiro et. al., 2008; Mkoma et. al., 2014). Thus, the ratio of acetate to formate (A/F) might be an indicator of the relative importance of direct emissions (high ratio) and in situ formation by photochemical processes (low ratio). Studies by Wang et. al., 2007; Mkoma et. al., 2012, Perola et. al., 2011 in Bogota, Sao Paulo and Buenos Aires reported that low ratio indicates photochemical formation of organic acids predominates.

The oxidation of biogenic or anthropogenic alkenes and in particular their ozonolysis has been suggested to be a major source of Formic acid and Acetic acid (Neeb et. al., 1997).

The vapor pressure of monocarboxylic acids is higher, by a factor of 10^2 to 10^4 than that of the corresponding dicarboxylic acids, the latter is likely to dominate in aerosol particles. Formic and acetic acids, the more abundant species in gaseous phase, are also found in aerosol particles collected in various areas of the world (Wang et. al., 2007; Khare et. al., 2011; Paulot et. al., 2011; Perola et. al., 2011; Frietas et. al., 2012; Mkoma et. al., 2012, 2014). Sanchez et. al., 2002 reported that the

behaviour of formic acid is not clearly resolved. Sometimes its concentration was higher in gas phase or sometimes in $PM_{2.5}$. On the other hand, acetic acid had a clearer pattern, its concentration in particulate matter was higher than gas phase. According to this study, the partition of the organic acids into liquid phase (e.g. cloud droplets or wet aerosols) is determined by the concurrence of various thermodynamic parameters such as: the vapor pressure, dissociation constant and Henry's law constant. This study suggested that the formic acid is more volatile than acetic acid. Mkoma et. al., 2014 observed in Brazil, propionate and acetate were the most abundant carboxylate ion in $PM_{2.5}$, accounted for 63% of the total mean analyzed carboxylates in day-time and 74% in night-time. The second most abundant carboxylate was formate which accounts for 13% in day-time and 9.5% at night-time of the total acids concentrations. Similar results were found for PM_{10}. Correlation analysis shows that they are mainly originated from burning of fossil fuel. According to Frietas et. al., 2012 in Londrina, Brazil, dicarboxylic acids in $PM_{2.5}$ contributed approximately 78% of total carboxylic acids at an urban site and 69% at a rural site. While monocarboxylic acids (Acetate and Formate) represented 22% and 31% of the total carboxylic acids in $PM_{2.5}$ at the urban and rural site, respectively. Mkoma et. al., 2012 reported acetate was most abundant in PM_{10} accounted for 62.5% of total carboxylates at a rural site in Tanzania. The concentrations of formate and acetate in Londrina (formate was 150 and 120 ng m^{-3} in PM_{10} and $PM_{2.5}$ respectively, acetate was 210 and 180 ng m^{-3} in PM_{10} and $PM_{2.5}$ respectively) were smaller than the concentrations found in São Paulo (concentration of formate and acetate was 480 and 430 ng m^{-3} respectively in $PM_{2.5}$) (Souza et. al., 1999). However, similar concentration level of formic acid in PM_{10} and $PM_{2.5,}$ 110 and 154 ng m^{-3} respectively was reported by Wang et. al., 2007 in Beijing, China. Similar level of carboxylic acids indicated that the traffic emission sources and the oxidation ability of the atmosphere were similar in both cities.

Although different studies have been conducted on ozone and its precursors (NOx, CO and VOCs). There are no reports which simultaneously present ozone forming process and ozone breakdown reactions. The present study is an attempt to bridge this gap. An attempt to use PCA (Principal Component Analysis) and ANN (Artificial Neural Network) will also be made to predict ozone levels.

OBJECTIVES

On the basis of literature review it is evident that there has been no systematic and simultaneous study of surface Ozone formation and its loss in the form of Organic acids.

With this in view the present study has been designed with the following objectives:

- To study the diurnal and seasonal trends of Ozone and its precursors (NO_x and CO).
- To determine the levels of some representative VOCs and study their seasonal trends.
- To explore the ozone loss processes through:

  Organic acids

  Black Carbon
- Modeling Ozone levels through PCA & ANN.

METHODOLOGY

SITE DESCRIPTION

The sampling will be carried out on the roof of Science Faculty, Dayalbagh Educational Institute. Dayalbagh (semi-urban site), Agra. Agra is located in the north central (27°10' N, 78°05' E) part of India which is about 200 km southeast of Delhi. It is a semiarid area characterized by loose, sandy, and calcareous soil prone to erosion. Vegetation is scarce and dominated by xerophytic plants. Climatically, Agra is hot and dry during the summer and cool in the winter. The annual rain fall is about 650 mm with 90% being received during monsoon season (July–September). Winter is associated with greater calm periods while during the summer and monsoon strong surface winds are observed. Maximum and minimum temperatures in summer are normally 45°C and 25°C, respectively, while in the winter it ranges between 10°C to 3°C. Relative humidity is highly variable from 25–99%.

Apart from the local sources Mathura refinery and Firozabad glass industries are both situated at a distance of 40 km from Agra. National Highway lies about 2 km from the sampling site. Although there are no industries in the immediate vicinity of the sampling site, during the monsoon, site becomes downwind with respect to the city's pollution sources.

O_3 and NOx Measurement

Surface O_3 and NOx concentrations will be recorded using continuously operating O_3 analyzer (Thermo Fischer Model 49i) and NOx analyzer (Thermo Fischer Model 42i).

The ozone concentration measurement is based on ultraviolet absorption photometry, the principle is that ozone (O_3) molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the ozone concentration as described by the Beer-Lambert law. Calibration of the system is done with the help of a built-in ozone generator. The sample is drawn through the sample bulkhead and is split into two gas streams. One gas stream acts as reference gas, flows to the reference solenoid valve. Other stream i.e. the sample gas, flows directly to the sample solenoid valve. The solenoid valves alternate every 10 seconds.

The NOx analyzer operates on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO_2 molecules decay to lower energy states.

Nitrogen dioxide (NO2) must first be transformed into NO before it can be measured using the chemiluminescent reaction. NO_2 is converted to NO by a molybdenum NO_2-to-NO converter heated to about 325 °C.

CO Measurement: Surface CO will be recorded using continuously operating CO analyzer (Model T300). The basic principle by which the analyzer works is called the Beer-Lambert Law. It defines how light of a specific wavelength is absorbed by a particular gas molecule over a certain distance. The T300 uses a high-energy heated element to generate a beam of broad-band IR light with a known intensity. This beam is directed through multi-pass cell filled with sample gas. The sample cell uses mirrors at each end to reflect the IR beam back and forth through the sample gas a number of times. The total length that the reflected light travels is directly related to the intended sensitivity of the instrument. Finally, the beam strikes a solid-state photo-detector that converts the light signal into a modulated voltage signal representing the attenuated intensity of the beam.

VOCs

Sampling will be carried out by active grab sampling method using a battery- operated pump. A battery operated portable sampling pump (SKC 224-XR) will be used to draw air at the rate of 2l min^{-1} through SKC adsorption cartridge containing activated charcoal (60–80 mesh). The sampling pump will be calibrated by an electronic digital flow calibrator. On an average 2 samples will be collected every week. Extraction of samples will be done in CS_2. Protection of the exposed charcoal tubes is a very important part of the VOC determination method. The sample tubes will be placed in polythene bags that seal tightly and kept in a box in a freezer until analysis. Analysis will be done by Shimadzu gas chromatograph (GC-17 A) equipped with a flame ionization detector (FID), BP1 capillary column (25m length and 0.3mm internal diameter), and GC Solution software. GC oven will programmed for 50ºC hold for 4min and ramped to 250ºC at a rate of 10ºC /min with 10min hold at 250ºC. N_2 will be used as carrier gas with 1 ml/min.

Organic Acids

Particulate HCOOH and CH_3COOH will be collected from the atmosphere using HVS Envirotech APM 550 Respirable Dust Sampler for the $PM_{2.5}$ and PM_{10}, operated at a flow rate of 16.6L/min for 24 hrs on 47 mm quartz microfiber filters (Pallflex,Tissuquartz) twice a week. From the loaded 47

mm quartz fibre filter paper one fourth will be cut for the analysis of water soluble organic acids. Before sampling, these quartz filters should be pre- heated at 900^{o}C for four hours. The exposed filters will be stored in refrigerator at 4°C before chemical analysis. Extraction of filters will be done in water. Samples will be analyzed by injected into the ion chromatograph (Dionex ICS-1100) using AS11 as analytical column and dilute solution of NaOH as eluent.

Meteorological parameters viz. solar radiation, temperature, relative humidity, rainfall, wind speed and wind direction were recorded at sampling site using Automatic Weather Station WM251 Data Logger at every 1-hr interval.

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